A SURVEY OF THE LITERATURE ON THE EXTRACTIVE METALLURGY AND ELECTROLYTIC REFINING OF BISMUTH

BY P. M. GRUZENSKY AND W. J. CRAWFORD

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SUMMARY

A survey of the literature has been made covering the extraction of bismuth from raw materials, its separation from lead, and its subsequent refining. The use of aqueous, nonaqueous, and fused electrolytes in electrolytic refining is reviewed.

This literature survey has been prepared preliminary to some proposed investigations concerning the electrometallurgy of bismuth, and, although an effort has been made to cover a majority of the applicable references, a critical review was not attempted and no assertion is made that this manuscript is exhaustive in nature.

Titles of publications in parenthesis are translations from the language in which the reference was originally published.

INTRODUCTION

Bismuth, atomic number 83, atomic weight 209, and specific gravity 9.82, belongs to Group V of the periodic table and has only 1 known stable isotope. It is the most metallic member of the group. Its common valence numbers are plus 3 and plus 5. It is a brittle metal and crystallizes in a rhombohedral face-centered or a deformed simple-cubic lattice.[1] It melts at 520° F. (271° C.), and it expands 3.3 percent by volume in changing from liquid to solid. Bismuth occurs principally as native metal and as the sulfide, bismuthinite.[2] Less common are the oxide bismite and the carbonate bismutite. It is also a minor constituent in a number of lead, copper, and tin ores. Its occurrence has been estimated to be of the same order as silver and tungsten.[3] A small amount of bismuth is recovered from ores mined chiefly for their bismuth content, but most of the bismuth produced is recovered as a byproduct from lead, copper, and tin refining.

The principal uses of bismuth are in low-melting alloys, alloys which expand upon cooling, and in pharmaceuticals and cosmetics. Recently the United States Atomic Energy Commission has shown an interest in certain low melting point bismuth alloys because of their low neutron-capture qualities.

1/ Liddell, D. M., Handbook of Nonferrous Metallurgy, Recovery of the Metals: McGraw-Hill Book Co., Inc., New York, N. Y., 1945, p. 139.
2/ Tyler, P. M., Bismuth: Bureau of Mines Inf. Circ. 6466, 1931, 19 pp.
3/ Smith, W. C., Bismuth and Bismuth Alloys, Encyclopedia of Chemical Technology: The Interscience Encyclopedia, Inc., New York, N. Y., vol. 2, 1948, p. 526.

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Attempts to roll bismuth into sheet and foil have not been successful. Bismuth wire has been produced by extrusion.4/ The freshly prepared wire can be coiled but becomes more brittle with age.

Information on 27 binary alloy systems containing bismuth has been compiled by the National Bureau of Standards. A selected and classified bibliography containing 246 references is included.5/

EXTRACTION OF BISMUTH

Liquation was one of the early methods used to extract bismuth from its ores. The process was carried out in inclined cast-iron pipes. The ore containing metallic bismuth was heated in the pipes, and bismuth flowed out of the bottom, leaving a residue that was still high in bismuth. This residue was smelted to a bismuthic speiss and then treated once again in the liquation furnaces.

The carbon reduction of bismuth-bearing ores has largely replaced the liquation process. The fusion can be carried out in crucibles or small reverberatory furnaces. Iron is added to effect decomposition of bismuth sulfide and suitable flux materials are added to form a fusible slag. The products, metallic bismuth, matte or speiss, and slag are separated after cooling in molds. The matte or speiss is resmelted for its bismuth content.

Wet extraction may be employed on ores that contain bismuth as the oxide or carbonate or on roasted tin concentrates. Finely crushed oxidized material is heated with hydrochloric acid for several hours to effect solution. The supernatant liquor is then diluted with water to precipitate bismuth oxychloride. Occluded lead chloride is washed out with hot water, and several reprecipitations are commonly carried out for purification. The bismuth oxychloride is then smelted with carbon and lime or soda ash. If the metal thus produced contains precious metals, it may be sent to the cupel furnaces for their recovery, and the oxidized bismuth again dissolved with hydrochloric acid. Bismuth produced by this method requires additional refining.

A new process for the beneficiation of bismuth sulfide ores6/ recently proposed by the University of Cluj, Romania, involves the chlorination of the pulverized ore at 550° C. Bismuth chloride distills from the mixture at 700° C. and is collected in glass condensers. The chloride is dissolved in dilute hydrochloric acid, is further treated to remove iron and copper, and the bismuth is recovered by displacement with iron on iron bars. Alternatively, the solution of the chloride may be used directly in the manufacture of bismuth subnitrate.

4/ Stockbarger, D. C., The Extrusion of Bismuth Wire: Jour. Opt. Soc. Am., vol. 14, 1927, p. 445.

5/ National Bureau of Standards, Bismuth: Circ. 382, 1930, 41 pp.

6/ Ripan, R., and Liteanu, C., (A New Procedure for the Preparation of Bismuth from Sulfide Ores): Acad. rep. populare romane, Bul. Stiint., Ser. Mat., Fiz., Chim. vol. 2, 1950, p. 257; Chem. Abs., vol. 45, 1951, p. 8949.

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SEPARATION FROM LEAD

Bismuth behaves similarly to lead in smelting. In roasting and slagging of copper ores, bismuth and lead are carried in the flue dust, and fumes and are collected in bag houses or Cottrell precipitators. These products are beneficiated at lead-smelting plants. During lead-smelting operations, bismuth in lead ores, concentrates, and flue dusts is collected in the lead bullion. Since commercial lead and bismuth must be relatively free of each other, respectively, their separation is of paramount importance. A number of methods have been applied to the "debismuthizing" of lead. These are described briefly.

Kroll-Betterton Process

Debismuthizing of lead by this process depends upon the formation of a calcium-bismuth dross when metallic calcium is introduced into molten lead. First studies on the process were carried out in Europe by Kroll[7] who subsequently patented it. Only limited development of the process was experienced on the continent because of the relatively limited availability of bismuth-lead and because the process yielded lead containing 0.02 percent bismuth, which was considered too high for high purity lead. Credit for developing the process commercially is due to J. O. Betterton of the American Smelting and Refining Co.[8] Cohn[9] has discussed the theory and economics of the process at length. In recent years[10] the process has been improved to the extent that the bismuth content of lead is reduced to 0.006 to 0.007 percent.

Crystallization Process

The melting points of lead, bismuth, and the lead-bismuth eutectic are 327°, 271° and 124° C., respectively. The eutectic contains 55.5 mole percent bismuth. Crystallization process is carried out in a long line of kettles. Molten lead containing bismuth is added to the central kettle, and the mass is colled slowly. Crystals of lead low in bismuth begin to settle out and are collected in a strainer and transferred to the kettle on the left while the remaining liquid, which is considerably higher in bismuth, is transferred to the kettle on the right. The process is continued in each kettle with the production of essentially pure lead at the left end of the row of kettles and rejection of high bismuth concentrate on the right end of the row of kettles. This is known as the Pattinson process and at one time was employed in debismuthizing as well as desilverizing of lead. The process now finds only limited application.

7/ Kroll, W., (Precipitation in Metallic Solution): Metall u. Erz, vol. 19, 1922, p. 317.

8/ Betterton, J. O., Metal Refining and Removing Bismuth from Lead: United States Patents 1,853,534; 1,853,535; 1,853,536; 1,853,537; 1,853,538; 1,853,539; 1,853,540; 1,853,541; Apr. 12, 1932.

9/ Cohn, R. F., Debismuthizing Lead With Calcium: Trans. Electrochem. Soc., vol. 59, 1931, p. 107.

10/ Evers, D., (Removal of Bismuth by the Kroll-Betterton Methods): Ztschr. Erzbergbau u. Metallhuttenw., vol. 2, 1949, p. 129.

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Betts Process[11]

Lead bullion containing at least 90 percent lead, the balance being silver, gold, bismuth, copper, antimony, arsenic, selenium and tellurium, is the starting point for this process. If more than 0.01 percent tin is present, it is first removed by a drossing procedure. Lead bullion anodes are cast and subjected to electrolysis in a lead fluosilicate and fluosilicic acid electrolyte. Pure lead is deposited on the lead cathode starting sheets. Glue or goulac is used as an addition agent. Current densities are of the order of 17 to 18 amperes per square foot. Impurities in the bullion anodes are insoluble and remain at the anode as a porous slime blanket. The anodes are withdrawn from the cells, and the slime blanket is scraped off, washed, dried, and melted to give metal and slag. The slag is usually purified and smelted to produce antimonial lead. The metal is melted and selectively oxidized to remove arsenic, antimony, and some lead. It is then transferred to the cupel furnaces and the oxidation continued until only "dore" containing the precious metals remains. The cupel slags, which are now rich in bismuth, are reduced with carbon to give impure bismuth metal and a copper matte. The bismuth is then sent to the refining plant. The Betts process at the present time is employed in leading lead refineries of the world.

Sperry Process[12]

This is a well known method for the manufacture of white lead. Bowman[13] has described some of the pioneer work in the development of the process. The process begins with desilverized lead anodes preferably containing some bismuth. Lead is dissolved at the anodes as electrolysis proceeds in a sodium acetate electrolyte. Carbon dioxide is bubbled into the electrolyte, which precipitates basic lead carbonate. No cathode deposit is formed. The anode impurities remain at the anode as a slime blanket. It is desirable to have a slime blanket that adheres to the anodes, otherwise impurities will drop off and contaminate the white lead. The slime blanket must be removed at frequent intervals to prevent the voltage from reaching a high value, which would effect electrolytic dissolution of metals other than lead. A bismuth-containing lead is to be desired for anode material since bismuth hardens the slime blanket and makes it more adherent. The slime produced by the process is washed, dried, and melted to an impure bismuth bullion, which is further processed at the bismuth refinery.

PYROMETALLURGICAL REFINING OF BISMUTH[14]

Impure bismuth, which is produced by the various methods already described, is melted and treated repeatedly with molten sodium hydroxide

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11/ Fingland, J. J., The Betts Electrolytic Lead-Refining Process in Practice: Trans. Am. Electrochem. Soc., vol. 57, 1930, p. 177.
12/ Sperry, E. A., White Lead: United States Patent 1,452,620, Apr. 24, 1923.
13/ Bowman, R. G., Pioneer Work in Development of White Lead Manufacture by Sperry Electrolytic Process: Eng. and Min. Jour., vol. 128, 1929, p. 318.
14/ See footnote 3.

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for the removal of arsenic and tellurium. The metal is cooled and a dross is skimmed off, which contains the copper. Silver and gold are next removed by extraction with zinc at a high temperature. The molten metal is stirred until all of the zinc has dissolved. It is then allowed to cool, and the zinc dross, carrying silver and gold, is skimmed off. The desilverized bismuth now contains only bismuth, lead, and zinc. Chlorine gas is bubbled through the molten metal at 500° C. Zinc is first chlorinated, then the lead. Chlorination is continued until the lead assay is reduced to 0.03 percent. Lead chloride slags are then removed and air blown through the molten metal until fuming stops, dross begins to form, and the surface of the metal indicates an oxide film. The metal is transferred to another kettle, again treated with molten caustic soda, and cast as refined bismuth. Bismuth metal refined by this process is 99.999 percent pure. Electrolytic refining processes have not been able to produce bismuth of this purity nor to operate as economically as the pyrometallurgical process described.

ELECTROLYTIC REFINING

Lacey[15] investigated the possibilities of separating silver from bismuth by electrolysis of binary alloys of the two metals. Alloys of different compositions were used for anodes, and investigations were carried out in silver cyanide and silver nitrate electrolytes. It was found that cathodic deposits of silver containing less than 1 percent bismuth could be obtained from the cyanide electrolyte. Maximum current density was 0.14 amperes per square decimeter. The silver deposits obtained from the silver nitrate electrolyte had high bismuth contents even at low current densities, and the results indicated no regularity.

Foerster and Schwabe[16] investigated the refining of bismuth in anode slimes from the Betts electrolytic lead process. They recommended the use of bismuth fluosilicate as electrolyte and reportedly obtained pure cathodic bismuth of a compact and dense nature from crude bismuth anodes containing silver and lead. They reported the deposition potentials of silver, bismuth, and lead in solutions of their fluosilicates to be far apart, silver remaining undissolved in the slimes and lead accumulating in the electrolyte. It is reported[17] that a Japanese company in 1929 refined bismuth from a fluosilicate electrolyte, producing about 260 pounds of pure bismuth daily, but no other data on the procedure were given. Harbaugh and Mathers[18] attempted to use a fluosilicate bath without success. Kern and Jones[19] investigated

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15/ Lacey, W. H., On the Electrolytic Refining of Silver-Bismuth Alloys: Trans. Am. Electrochem. Soc., vol. 22, 1912, p. 301.

16/ Foerster, F., and Schwabe, E., (Electrolytic Refining of Bismuth): Ztschr. Elektrochem., vol. 16, 1910, p. 279.

17/ Shiga, Kiyoshi, Cottrell Electrical Precipitation Processes in Japan: Eng. and Min. Jour., vol. 128, 1929, p. 86.

18/ Harbaugh, M., and Mathers, F. C., The Electrodeposition of Bismuth From Perchloric Acid Solutions: Trans. Electrochem. Soc., vol. 64, 1933, p. 293.

19/ Kern, E. F., and Jones, T. R., Addition Agents in Bismuth Electrolytes: Trans. Am. Electrochem. Soc., vol. 57, 1930, p. 255.

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several electrolytes for the purification of bismuth. Their work with a fluosilicate electrolyte gave a very spongy cathode deposit while a thick deposit of oxy-salt covered the anode. Current densities employed in their work were appreciably higher than those reported by Foerster and Schwabe. They concluded that bismuth was not soluble enough in fluosilicic acid to warrant its use as an electrolyte. Other electrolytes investigated by Kern and Jones and the results obtained are as follows:

The use of a fluoboric acid electrolyte containing 122 grams HBF_4 per liter gave a spongy cathode deposit and a dense white anode deposit of oxy-salt. They concluded that bismuth anodes do not dissolve enough in fluoboric acid to be of interest in electrolytic work.

The use of cresol-sulfonic acid was unsatisfactory. A limited spongy deposit was produced at the cathode and a voluminous white deposit formed at the anode. Of all the acids tried, bismuth seemed to be least soluble in cresol-sulfonic acid solution.

When perchloric acid was used as electrolyte, voluminous sponge metal was deposited on the cathode. The anode remained clean and smooth and dissolved anodically until the bismuth concentration in the electrolyte was built up to an upper limit at which time a heavy white oxy-salt was deposited on the anode.

The use of a double fluoride of bismuth and sodium in hydrofluoric acid as an electrolyte was eliminated because of the insolubility of sodium fluoride in hydrofluoric acid.

A sulfuric acid solution of bismuth trichloride gave a slight, powdery, nonadherent deposit at the cathode and a heavy white basic salt at the anode. Modification of this electrolyte by addition of sodium sulfate or magnesium sulfate indicated no advantages.

Hydrochloric acid solutions of bismuth trichloride containing sodium chloride, calcium chloride, or magnesium chloride were found to give cathode deposits of bring metallic sponge, which broke more or less to a powder when touched. No oxysalts were deposited at the anode and considerable anodic corrosion took place. Glue, goulac, gum arabic, benzoic acid, resorcin, hydroquinone, pyrogallol, tannic acid, and aloes Curacoa were tried as addition agents with the hydrochloric acid electrolytes. It was concluded that satisfactory deposits could be obtained from these electrolytes. All of the work of Kern and Jones was carried out at a current density of 15 amperes per square foot.

Mohn[20/] has described lead and bismuth refining operations at a plant in Mexico. Lead was first separated by the Betts process. Bismuth was refined electrolytically using a 10-percent hydrochloric acid solution containing 7 percent bismuth trichloride for electrolyte. Cathode current

20/ Mohn, A., Electrolytic Refining of Bismuth: Electrochem. and Met. Ind., vol. 5, 1907, p. 314.

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density was 20 amperes per square foot. Bismuth analyzing 99.8 percent pure was obtained, the chief impurity being silver.

The work of Wohlwill[21] and Borchers and Stahlmann[22] indicates that in the electrorefining of bismuth with an electrolyte containing 100 grams hydrochloric acid and 70 to 100 grams bismuth per liter, the potential drop should not exceed 0.15 volt to avoid codeposition of silver and lead.

Levin[23] reported the use of a double chloride of sodium and bismuth as electrolyte for the bismuth plating of iron. Shiny, finely crystalline coatings were obtained at a current density of 2 to 2.7 amperes per square decimeter. The electrolyte contained 70 to 100 grams bismuth salt and 200 to 300 cc. concentrated hydrochloric acid per liter. Glue was used as addition agent.

Mathers[24] found that bismuth, which was deposited from acidified chloride or bromide solutions contained 0.3 and 7 to 11 percent of the respective halogens.

Prior[25] reviewed the literature on electrolytic refining of bismuth and demonstrated experimentally the conditions for practical refining. He reported a suitable electrolyte to contain 100 grams of bismuth as chloride and 100 grams of free hydrochloric acid per liter. Good deposits were obtained with current densities up to 200 x 10^{-4} amperes per square centimeter. The current efficiency was 95 to 98 percent.

Deposition of bismuth from perchloric acid solutions was investigated by Harbaugh and Mathers.[26] They recommended a plating bath containing 4 grams of bismuth trioxide and 10.4 grams of perchloric acid per 100 cc. of solution with 0.03 percent glue and 0.08 percent cresol as addition agents. The presence of small quantities of nitric acid or ammonium nitrate or of large quantities of ammonium perchlorate had no appreciable effect on the deposit. They stated that, owing to the characteristics of electrodeposited bismuth, its plating on base metals for ornamental or protective purposes seemed unsatisfactory. They indicated that the coating might be found of

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21/ Wohlwill, H., (Electrolysis in Recovery and Refining): Metall u. Erz, vol. 29, 1932, p. 1.

22/ Borchers, H., and Stalmann, G., (Effect of Colloids, Current Density, and Temperature on the Physical Properties of the Cathode Deposit and Current Efficiency in the Electrolysis of Bismuth): Metall u. Erz, vol. 33, 1936, p. 94.

23/ Levin, A. I., (Bismuth Electroplating): Jour. Applied Chem. (U.S.S.R.), vol. 17, 1944, p. 613.

24/ Mathers, F. C., Complex Cations as the Important Influence in Plating Baths: Proc. Am. Electroplaters' Soc., June, 1939, p. 134.

25/ Prior, Karl, Uber die elektrolytische Raffination des Wismuts: Universitatsverlag von Robert Noske in Borna-Leipzig, 1928 (doctorate dissertation).

26/ See footnote 18.

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value in certain electrical or other physical devices. It was concluded that the perchlorate electrolyte was unsatisfactory for refining bismuth but could be used with satisfaction for the deposition of alloys of bismuth, lead, and arsenic. The deposited bismuth was found to contain some perchlorate and addition agent.

Fink and Gray[27] investigated the codeposition of lead and bismuth from a perchloric acid electrolyte in a search for corrosion resistant lead alloys. They found that the percentage of lead in the deposited alloy increased with increasing current density and that at very low current density bismuth deposited alone. The recommended electrolyte for alloy deposition was 9 grams of lead, 9 grams of bismuth, 93 grams of perchloric acid, and 5 drops of oil of cloves per liter. Current densities were 1.2 to 3.6 amperes per square foot. Smooth, adherent deposits were obtained.

Heberlein[28] in a review of progress in electrolytic refining stated that bismuth has been refined more or less successfully with the aid of electrolytes composed principally of nitric acid, perchloric acid, fluosilicic acid, or hydrochloric acid. A fluosilicate electrolyte may be advantageous because of the virtually complete insolubility of silver, but its higher reagent cost makes it uneconomical compared with hydrochloric acid electrolyte.

Piontelli[29] has made a comparison of current efficiencies, purity and conditions of deposition in the electrolytic refining of bismuth from strongly acid electrolytes of fluosilicate, fluoborate, perchlorate, and chloride. He reported that for protective and ornamental deposits, perchlorate is preferred, and the other solutions mentioned are used for the preparation of bismuth of high purity. Of these, the chloride solution has the advantage of lower cost, higher conductivity, and greater stability at varying temperatures, whereas, from fluoborate solutions, the best deposits are obtained even at very high current densities. In all cases high current efficiencies are obtained.

Betts[30] stated that an excellent electrolyte for refining bismuth is a solution containing about 10 percent free methyl sulfuric acid and 4 percent bismuth as methyl sulfate.

Sand[31] carried out numerous experiments on electroanalytical deposition and separation of metals and reported that satisfactory results could be obtained in the deposition of bismuth from acetate, tartrate and nitrate solutions. He noted that the potential of the cathode had to be kept as low as possible.

27/ Fink, C. G., and Gray, O. H., Codeposition of Lead and Bismuth: Trans. Electrochem. Soc., vol. 62, 1932, p. 123.

28/ Heberlein, M. F. W., Progress in Electrolytic Refining of Metals: Trans. Electrochem. Soc., vol. 77, 1940, p. 119.

29/ Piontelli, R., (Electrolytic Refining of Bismuth): Atti X° congr. intern. chim., vol. 3, 1939, p. 609.

30/ Betts, A. G., Lead Refining by Electrolysis: John Wiley & Sons, New York, N. Y., 1908, p. 89.

31/ Sand, H. J. S., Deposition and Separation of Metals: Jour. Chem. Soc., vol. 91, pt. 1, 1907, p. 394.

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Jilek and Lukas[32] stated that bismuth could be separated and deposited as coherent lustrous layers at a current density of 0.1 ampere per square decimeter if specified amounts of fluoboric acid or sucrose were present in the electrolyte. They found further[33] that a weighable deposit could be obtained from a solution containing not more than 0.3 gram of bismuth, 3 cc. of nitric acid, and 8 grams of sodium tartrate per 100 cc. of solution.

Collin[34] described the electrolytic separation of lead and bismuth by using controlled cathode potentials in connection with electroanalysis. A nitric acid solution of the two metals was used.

Brunck[35] reported that bismuth could be determined electroanalytically by cathodic deposition from a nitric acid solution, but that the method was not satisfactory for a quantitative separation of lead and bismuth.

Kammerer[36] reviewed the early literature and found that numerous and diverse methods have been proposed for the quantitative deposition of bismuth from various electrolytes. He stated that bismuth has been deposited from solutions of oxalic acid, ammoniacal citrate, nitric acid, sulfuric acid, and phosphoric acid. Also mixed electrolytes containing alkaline phyrophosphates, carbonates, and oxalates have been employed. He found that it was possible to deposit bismuth in a compact form from an electrolyte containing nitric acid, sulfuric acid, and potassium sulfate.

One of the greatest difficulties encountered in the electrolytic determination of bismuth is a black, spongy, nonadherent cathode deposit and simultaneous deposit of bismuth peroxide on the anode. Metzger and Beans[37] found that the addition of acetic acid to a bismuth nitrate solution prevented peroxide formation at the anode. They further reported that if boric acid is also present in the electrolyte, a smooth, compact, adherent deposit having the characteristic color of the metal is obtained.

Smith[38] has reported conductivity measurements and electrode potentials of bismuth in nitric and perchloric acids.

32/ Jilek, A., and Lukas, J., (Separation of Bismuth by Rapid Electrolysis in Acid Solutions): Chem. Listy, vol. 21, 1927, p. 49.

33/ Lukas, J., and Jilek, A., (Electrolytic Deposition of Bismuth by Means of Reduced Potential): Chem. Listy, vol. 21, 1927, p. 541.

34/ Collin, E. M., The Electrolytic Separation of Lead and Bismuth With Controlled Potential: Analyst, vol. 54, 1929, p. 654.

35/ Brunck, O., Electrolytic Determination of Bismuth: Jour. Chem. Soc., vol. 82, pt. 2, 1902, p. 478.

36/ Kammerer, A. L., The Electrolytic Estimation of Bismuth and its Separation From Other Metals: Jour. Am. Chem. Soc., vol. 25, 1903, p. 83.

37/ Metzger, F. J., and Beans, H. T., The Electrolytic Determination of Bismuth: Jour. Am. Chem. Soc., vol. 30, 1908, p. 589.

38/ Smith, D. F., The Condition of Bismuth Salts in Aqueous Solutions and the Molal Electrode Potential of Bismuth: Jour. Am. Chem. Soc., vol. 45, 1923, p. 360.

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NONAQUEOUS ELECTROLYSIS

Patten and Mott[39] reported the deposition of bismuth from a solution of the trichloride in acetone at a moderately low current density.

Plotnikov and Gorenbein[40] stated that bismuth was deposited from a solution containing bismuth bromide 6.17 percent, aluminum bromide 13.36 percent, and nitrobenzene 80.47 percent. Conductivity measurements and decomposition potentials were given.

Schmidt[41] found that bismuth could be deposited from an anhydrous acetic acid solution of the chloride. A cathodic bismuth deposit also was obtained by using a bismuth anode and an anhydrous acetic acid electrolyte containing 7 percent potassium fluoride.

Kahlenberg[42] reported that the deposition of bismuth from an anhydrous solution of bismuth trichloride in methyl alcohol yields a poorly adherent, black, spongy powder.

FUSION ELECTROLYSIS

One of the problems encountered in fusion electrolyses is the solubility of the deposited metal in the fused electrolyte.

In the electrolysis of molten bismuth trichloride no metal regulus is obtained.[43] Bismuth trichloride melts at a low temperature to a clear liquid, which, upon electrolysis, immediately becomes dark colored, and only at the anode surface where chlorine is evolved does the bath remain clear. The solidified melt is entirely permeated with bismuth, and the crystal mass has a metallic luster.

Drossbach[44] electrolyzed fused bismuth trichloride at 340° C. for 16 hours. Bismuth metal at a 49.3-percent yield was produced. He reported that the nature of the bismuth trichloride - bismuth phase diagram requires prolonged electrolysis before metallic bismuth is obtained.

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Cleary and Cubicciotti[45] reported the solubility of bismuth in molten bismuth trichloride to be 47.3 mole percent at 450° C. They investigated the effect of the addition of other salts on its solubility and found that with salts of metals of about the same electropositiveness, the larger the anion to cation ratio, the less effective the salt in reducing solubility of the metal. For salts of the same anion to cation ratio, the more electropositive the metal of the cation, the more effective was the salt in reducing the solubility of bismuth.

Griffith and Mallett[46] have reported the solubility limits of oxygen and carbon in liquid bismuth at various temperatures and describe analytical methods for their determination.

Morris, Douglas, and Vaughn[47] investigated the electrodeposition of bismuth from molten bismuth trioxide in a carrier salt of sodium chloride-calcium chloride eutectic. Purity of the product obtained was as high as 99 percent bismuth. Energy consumption was low. The authors claimed the process to be commercially feasible.

Dittmer[48] has patented a process for removing bismuth from impure lead consisting of electrolyzing the molten impure metal cathode in a molten sodium hydroxide electrolyte at 330° to 350° C. at a cathode current density of 100 to 400 amperes per square foot and an anode current density of 200 to 1,000 amperes per square foot. Bismuth is transferred from the cathode to the anode, which consists of an iron pan containing molten lead. No explanation is given for the mechanism of this unique process, which is contrary to the usual electrochemical process wherein metal is dissolved at the anode and deposited at the cathode.

Wehrman and Yntema[49] and Verdieck and Yntema[50] reported the deposition potentials of bismuth and other metals in fused aluminum halide baths as measured with an aluminum reference electrode.

45/ Cleary, G., and Cubicciotte, D., The Solubility of Bismuth in Mixtures of Bismuth Chloride With Other Chlorides: Jour. Am. Chem. Soc., vol. 74, 1952, p. 557.

46/ Griffith, C. B., and Mallett, M. W., The Solubility of Carbon and Oxygen in Liquid Bismuth: Jour. Am. Chem. Soc., vol. 75, 1953, p. 1832.

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48/ Dittmer, J. C., Process for the Electrolytic Refining of Lead or Lead Alloys Containing Bismuth: United States Patent 2,507,096, May 9, 1950.

49/ Wehrman, R., and Yntema, L. F., The Electrochemistry of Baths of Fused Aluminum Halides, III: Jour. Phys. Chem., vol. 48, 1944, p. 259.

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Delimarskii, Berenblyum, and Sheiko[51] measured the electrode potentials of various metals in a fused sodium chloride-aluminum chloride bath. They reported the deposition potential of bismuth to be 0.65 volt.

Hurley and Wier[52] have shown that bismuth can be deposited from a solution of its chloride in molten ethyl pyridinium bromide.

51/ Delimarskii, Y. K., Berenblyum, L. S., and Sheiko, I. N., (Determination of Electrode Potentials in Fused Aluminum Chloride-Sodium Chloride as Solvent): Zhur. Fiz. Khim., vol. 25, 1951, p. 398.

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